

Temperature driven α to β phase-transformation in Ti, Zr and Hf from first principles theory combined with lattice dynamics

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Lattice dynamical methods used to predict phase transformations in crystals typically deal with harmonic phonon spectra and are therefore not applicable in important situations where one of the competing crystal structures is unstable in the harmonic approximation, such as the bcc structure involved in the hcp to bcc martensitic phase transformation in Ti, Zr and Hf. Here we present an expression for the free energy that does not suffer from such shortcomings, and we show by self consistent *ab initio* lattice dynamical calculations (SCAILD), that the critical temperature for the hcp to bcc phase transformation in Ti, Zr and Hf, can be effectively calculated from the free energy difference between the two phases. This opens up the possibility to study quantitatively, from first principles theory, temperature induced phase transitions.

Martensitic phase transformations are common, both in alloys frequently used in industry, such as shape memory alloys [1], and in the elemental group 3 to 4 transition metals [2], not to mention martensitic transformation in iron and iron-based alloys, a crucial phenomenon for metallurgy [3]. Thus there exists a substantial interest both from an industrial, applied and an academic point of view to develop accurate and effective methods to understand and even predict martensitic phase-transformations.

The hcp to bcc (or α to β) transition in Ti, Zr and Hf is a martensitic phase transformation that has been thoroughly investigated both from an experimental [2, 4] and theoretical [5–8] perspective. Recently Hennings *et al* developed and used a classical potential of the modified embedded atom method (MEAM) [9] to accurately reproduce the phase boundary between the hcp and bcc structure in Ti. However, there is up to this date a lack of first principles theoretical studies made of the martensitic hcp to bcc phase-transformation in Ti, Zr and Hf. The problem is that anharmonic effects in lattice dynamics [10] are of crucial importance for finite-temperature structural phase transitions, and their quantitative first-principle treatment is a real challenge.

A straightforward calculation using DFT molecular dynamics (DFT-MD)[11] should in principle be able to reproduce the bcc to hcp phase transformation in Ti and similar materials, since DFT-MD implicitly include anharmonic effects. However, DFT-MD is a computationally very demanding task which makes its use problematic. Instead we will here exploit the method of self consistent *ab initio* lattice dynamical calculations (SCAILD) [12]. Here, we further develop this method in order to be able to calculate *thermodynamic* properties, such as structural free energy difference (before we were restricted by the calculations of temperature-dependent

phonon frequencies only [12–16]). Since the SCAILD scheme is a constrained sampling method, in that it only samples the lattice dynamical phase-space along the normal mode directions of commensurate phonons [12, 13], the SCAILD calculations are much faster and, thus, much more practical than the corresponding DFT-MD calculations.

Thus, we propose here a new expression of the free energy of the SCAILD scheme, and we show that from the atomic configurations and the phonon density of states produced by the SCAILD calculations, an accurate measure of the free energy for the different phases can be obtained.

In order to properly describe temperature driven phase transformations in general, one must include the interaction between phonons [10]. As a result, phonon frequencies turn out to be temperature dependent which we explore numerically in this study by means of the SCAILD method [12–16].

The SCAILD method is based on the calculation of Hellman-Feynman forces of atoms in a supercell. The method can be viewed as an extension of the frozen phonon method [17], in which all phonons with wave vectors \mathbf{q} commensurate with the supercell are excited together in the same cell by displacing atoms situated at the undistorted positions $\mathbf{R} + \mathbf{b}_\sigma$, according to $\mathbf{R} + \mathbf{b}_\sigma \rightarrow \mathbf{R} + \mathbf{b}_\sigma + \mathbf{U}_{\mathbf{R}\sigma}$, where the displacements are given by

$$\mathbf{U}_{\mathbf{R}\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q},s} \mathcal{A}_{\mathbf{q}s}^\sigma \epsilon_{\mathbf{q}s}^\sigma e^{i\mathbf{q}(\mathbf{R}+\mathbf{b}_\sigma)}. \quad (1)$$

Here \mathbf{R} represent the N Bravais lattice sites of the supercell, \mathbf{b}_σ the position of atom σ relative to this site, $\epsilon_{\mathbf{q}s}^\sigma$ are the phonon eigenvectors corresponding to the phonon mode, s , and the mode amplitude $\mathcal{A}_{\mathbf{q}s}^\sigma$ is calculated from

the different phonon frequencies $\omega_{\mathbf{q}s}$ through

$$\mathcal{A}_{\mathbf{q}s}^\sigma = \pm \sqrt{\frac{\hbar}{M_\sigma \omega_{\mathbf{q}s}}} \left(\frac{1}{2} + n_{\mathbf{q}s} \right), \quad (2)$$

where $n_{\mathbf{q}s} = n(\frac{\omega_{\mathbf{q}s}}{k_B T})$, with $n(x) = 1/(e^x - 1)$, are the phonon occupational numbers, M_σ the atomic masses and T is the temperature of the system. The phonon frequencies, $\omega_{\mathbf{q}s}$, are defined through the variational derivative of the total energy with respect to the occupation numbers

$$\begin{aligned} \hbar \omega_{\mathbf{q}s} &= \frac{\delta E_{tot}}{\delta n_{\mathbf{q}s}} = \\ \sum_\sigma \frac{\delta E_{tot}}{\delta \mathcal{A}_{\mathbf{q}s}^\sigma} \frac{\delta \mathcal{A}_{\mathbf{q}s}^\sigma}{\delta n_{\mathbf{q}s}} &= -\frac{\hbar}{\omega_{\mathbf{q}s}} \sum_\sigma \frac{\epsilon_{\mathbf{q}s}^\sigma \cdot \mathbf{F}_{\mathbf{q}}^\sigma}{\mathcal{A}_{\mathbf{q}s}^\sigma M_\sigma}, \end{aligned} \quad (3)$$

obtained through the Fourier transform $\mathbf{F}_{\mathbf{q}}^\sigma$ of the forces acting on the atoms in the supercell.

Due to the simultaneous presence of all the commensurate phonons in the same force calculation, the interaction between different lattice vibrations are taken into account and the phonon frequencies given by Eq. (3) are thus renormalized by the very same interaction.

By alternating between calculating the forces on the displaced atoms and calculating new phonon frequencies and new displacements through Eqs. (1)-(3) the phonon frequencies are calculated in a self consistent manner. For more details on the SCAILD method we refer to Refs. 12–14. It should be mentioned that we do not consider here the phonon decay processes (see, e.g., Ref. 18 and references therein).

The free energy as a function of volume, V , and temperature for the bcc and hcp structures can be calculated through the expression

$$F(T, V) = U_0(V) + F_{ph}(V, T) + F_{el}(V, T), \quad (4)$$

where U_0 is the static ground state energy of the respective structures at $T = 0$ K (i.e without any phonons excited and temperature excitations of electronic states), F_{ph} is the free energy of the phonons and F_{el} is the free energy of the electrons. The temperature dependent parts of the free energy can be found as

$$\begin{aligned} F_{ph}(V, T) + F_{el}(V, T) = \\ \frac{1}{N_I} \sum_{\{\mathbf{U}_{\mathbf{R}}\}} \Delta F^*(\{\mathbf{U}_{\mathbf{R}}\}, V, T) + \frac{3}{2} k_B T - T S_{ph}(V, T). \end{aligned} \quad (5)$$

Here ΔF^* is the change in free energy relative to the ground state energy U_0 , caused by the phonon induced atomic displacements described by Eq. (1), and thermal excitations of the electronic states. The sum on the right-hand part of Eq. (5) is over the different atomic configurations, $\{\mathbf{U}_{\mathbf{R}}\}$, generated throughout the SCAILD self consistent run. Since ΔF^* are calculated at atomic configurations accommodating the different frozen phonon

superposition of Eq. (1), ΔF^* not only contains the finite temperature contribution to the electronic free energy for a given atomic configuration, but also, the potential energy provided by the frozen lattice waves, i.e the potential energy of the phonons at a particular phonon superposition [19]. The phonon kinetic energy is given by $3k_B T/2$ per atom which means that atomic motion is considered as classical; typically, temperatures of structural phase transformations are higher than the Debye temperature, thus, this approximation is well justified.

In practice, the sum of the finite temperature electron free energy and phonon potential energy, ΔF^* , was obtained by calculating the total free energy of the corresponding atomic configuration using a Fermi-Dirac temperature smearing of the Kohn-Sham occupational numbers [20], and then subtracting the static potential energy U_0 (Here U_0 is calculated with the tetrahedron method to provide a good reference to the temperature excited electronic states). The number of configurations, N_I , used for each volume and temperature was typically 400.

Another problem is how to calculate the phonon entropy. We will assume that it depends on the phonon occupation numbers $n_{\mathbf{q}s}$ in the same way as for noninteracting bosons:

$$S_{ph} = k_B \sum_{\mathbf{q}s} [(1 + n_{\mathbf{q}s}) \ln(1 + n_{\mathbf{q}s}) - n_{\mathbf{q}s} \ln n_{\mathbf{q}s}] \quad (6)$$

This is the only entropy expression consistent with Eq. (2) and (3), which can be proved in the exact same manner as was done for fermions in the Landau theory of a normal Fermi liquid [21]. Thus the SCAILD scheme, together with a free energy defined through Eqs. (5) and (6), constitutes nothing but a theory of a “normal Bose liquid”. Expression (6) can be written in terms of the phonon density of states, $g(\omega)$, produced by a converged SCAILD calculation, and is given by

$$\begin{aligned} T S_{ph}(V, T) = \\ \int_0^\infty d\omega g(\omega, V, T) \hbar \omega \left[n\left(\frac{\hbar \omega}{k_B T}\right) - \frac{k_B T}{\hbar \omega} \ln \left(1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \right]. \end{aligned} \quad (7)$$

Here the phonon frequencies used to calculate the phonon density of states, $g(\omega)$, are the normal mode configurational mean values

$$\langle \hbar \omega_{\mathbf{q}s} \rangle = \frac{1}{N_I} \sum_{\{\mathbf{U}_{\mathbf{R}}\}} \frac{\delta E_{tot}(\{\mathbf{U}_{\mathbf{R}}\}, V, T)}{\delta n_{\mathbf{q}s}}. \quad (8)$$

It should be stressed that the partitioning of the free energy through Eqs. (4), (5) and (7) has been chosen to maximize both the accuracy of the phonon potential energy, which in the form of Eqn.(5) take into account anharmonicity up to infinite order, and the phonon entropy, which in the form given by Eqn.(7) is accurate to leading order in anharmonic perturbation theory [22].

The phonon density of states and the corresponding free energies for the hcp and bcc structures were calculated at up to five different temperatures, and at each temperature, SCAILD calculations were performed at up to five different volumes. As an example of the typical data obtained from the calculations, the resulting Titanium free energies obtained through Eq. (5), are shown in Fig. 1.

As regards the other computational details of the force calculation we used the VASP package [20], within the generalized gradient approximation (GGA). The projector-augmented wave (PAW) potentials required energy cutoffs of 232 eV. The Ti(4s,3d), Zr(4s,4p,5s,4d) and Hf(6s,5d) levels were treated as valence electrons. The k-point mesh was a $5 \times 5 \times 5$ Monkhorst-Pack grid in the bcc phase calculations. In the hcp phase calculations $6 \times 6 \times 6$ gamma centered mesh was used. In order to include the electron entropy in the calculations, Fermi-Dirac temperature smearing were applied to the Kohn-Sham occupational numbers. The bcc and hcp supercells used were obtained by increasing the bcc primitive cell 4 times and the hcp primitive cell 3 times, along the respective bcc and hcp primitive lattice vectors. The sizes of the supercells were chosen such that to ensure a sufficient decay of the interatomic force constant within the supercell, permitting a proper sampling of the lattice dynamical phase space [23]. For the calculations of the static potential energy, U_0 in Eqn.(4), the all-electron full-potential linearized augmented-plane wave (FP-LAPW) package ELK [24] was used within the GGA approximation. This was found necessary to ensure a high accuracy of the zero temperature part of the bcc - hcp energy difference. An energy cutoff of 270 eV together with a $24 \times 24 \times 24$ k-point mesh and a $24 \times 24 \times 15$ k-point mesh were used for the bcc and hcp structures, respectively, in these calculations the Methfessel-Paxton integration scheme was used with a 0.2 eV smearing of the Kohn-Sham eigenvalues.

For each temperature the free energy obtained through Eq. (5) was fitted to a first order polynomial in V (for typical data see Fig. 1). Then by using these first order fits together with Eq. (4), the total free energy at each temperature was obtained through minimization with respect to volume. In Fig. 2(a), (c) and 3 (a), the minimized free energy at each temperature is displayed for the bcc and hcp structure in Ti, Zr and Hf, respectively. In Fig. 2(b), (d) and 3 (b) the free energy difference between the structures is displayed for Ti, Zr and Hf, respectively.

The temperature driven hcp to bcc phase-transition in Ti can be seen to occur at $T \sim 1100$ K, which is reasonably close to the experimentally observed phase transition temperature of 1155 K [26], whereas in Zr and Hf, the transition is predicted to occur at $T \sim 920$ K and $T \sim 1660$ K, respectively. The theoretical estimates of the transition temperature in Zr and Hf, with their respective experimental data of 1135

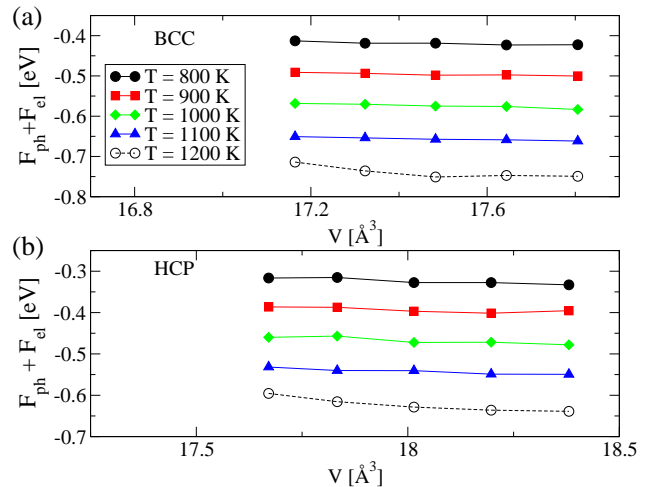


FIG. 1: (Color online) The calculated free energy at different volumes and temperatures for Ti in the bcc phase (a), and the hcp phase (b).

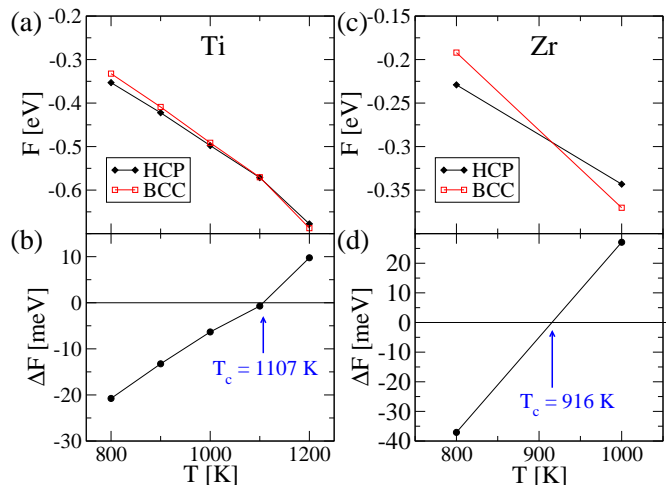


FIG. 2: (Color online) In (a) and (c) the calculated free energy of the bcc and hcp phase, in Ti and Zr, respectively. In (b) and (d) the calculated free energy difference, $\Delta F = F_{hcp} - F_{bcc}$, in Ti and Hf, respectively

K and 2015 [2], does not correspond to experimental data as well as in the case of Ti, however, given that first principles calculations (at $T = 0$), with current exchange and correlations functionals, have a problem in resolving energy differences between different crystallographic phases better than ~ 10 meV/atom, one may not expect from any first principles based theory, like the SCAILD method used here, to reproduce temperature induced phase transitions with an accuracy better than a few hundred Kelvin.

It should be noted here that the presently used free energy expression differs significantly from the previously

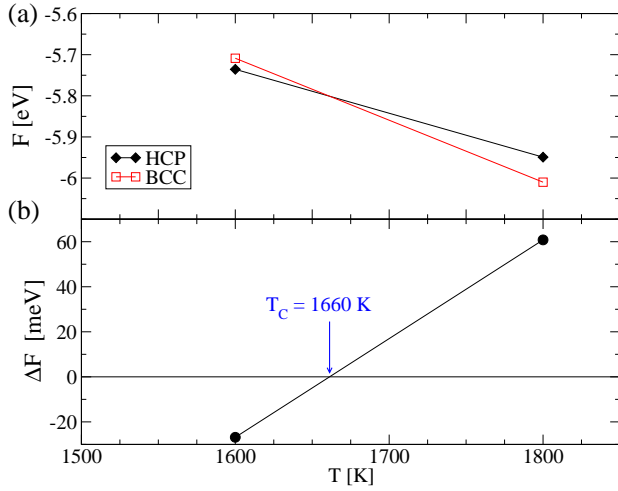


FIG. 3: (Color online) In (a) the calculated free energy in Hf for the bcc and hcp phase represented by red empty squares and filled black diamonds, respectively. In (b) the calculated free energy difference in Hf, $\Delta F = F_{hcp} - F_{bcc}$.

used expression from quasi-harmonic theory (e.g. used in Ref.[13]) in that it takes into account the anharmonic contributions to the lattice dynamical potential energy without projecting it down on a quasi-harmonic description as in Ref.[13]. In fact, using the old free energy expression together with the first principles inter atomic forces calculated in this work, results in the hcp phase in Ti being ≈ 90 meV lower in free energy compared to the free energy of the bcc phase throughout the entire temperature interval $800\text{K} < T < 1200\text{K}$.

In summary, we introduce here an expression for the free energy which is applicable also for highly anharmonic crystals. The free energy expression can readily be interfaced with lattice dynamic methods, for instance the SCAILD technique, and we show that the temperature induced hcp \rightarrow bcc transition of Ti, Zr and Hf can be reproduced by theory. Theory puts the transition temperature in Ti, Zr and Hf to 1100 K, 920 K and 1660 K, respectively.

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